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# New PBX 9501 Dynamic Mock Candidates via the Wet Slurry Process

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## Abstract

Novel PBX 9501 dynamic mock candidates were produced via the wet slurry process. The material selection criteria and development processes are detailed.

## Introduction

Development of new processes or devices can be a difficult and time-consuming proposition with the easiest of materials; even more challenges arise when the material is explosive. Safety concerns dictate that development cannot always proceed with an explosive, so a stand-in, or mock material, is required. Because no single mock material possesses all the characteristics of the material it emulates, most mocks are designed with one characteristic of the real material to emulate: density, weight, viscosity, thermal conductivity, etc. Thirty-three mock materials are currently approved for use at LANL.<sup>1</sup> Only one of these, Mock 900-31 (a mock for PBX 9501), is listed as a dynamic mock: a mock that behaves the same as the real material under dynamic mechanical and rheological conditions. Previous research improved upon this mock by preparing it in molding powder form that meets granular specifications of real PBX 9501, but left the composition unchanged.<sup>2</sup>

Because Mock 900-31 is a sucrose-based material, problems arose when it was subjected to temperatures and pressures outside of the original design space, including moisture regain, caramelization, and compaction. For these reasons, a new dynamic mock for PBX 9501 with a wider working range of conditions was required.

## Results and Discussion

Design of the new dynamic PBX 9501 mock began with a list of requirements for candidate materials:

1. The base material shall not be a hydrate (to avoid structural changes when water boils off above 100 °C).
2. The material must have a white to off-white color to allow for dyes to be added. (This was not an initial consideration so several colored mock material candidates were prepared)
3. The base material must have a melting point above 200 °C to expand the thermal window above the sucrose-based Mock 900-31.
4. The base material must be available and inexpensive in large quantity.
5. The material shall not be hygroscopic and is preferred to be water insoluble.
6. Preferably, the base material shall be available in a variety of particle size distributions, will not have a needle, plate, or leaflet habit, and shall be of monoclinic or higher crystalline symmetry.
7. Preferably, the base material will have a low toxicity and environmental impact to facilitate use by workers and disposal of wastes.
8. Preferably, the base material will have a density close to 1.905 g/cm<sup>3</sup>

An exhaustive search of inorganic and organic compounds listed in the *CRC Handbook of Chemistry and Physics*,<sup>3</sup> *Lange's Handbook of Chemistry*,<sup>4</sup> and *Perry's Chemical Engineer's Handbook*<sup>5</sup> was conducted to capture common

compounds, and a list of over 200 potential candidates was compiled. Of these, three inorganic and twenty-four organic substrates were downselected for examination based on the criteria above (Table 1). Most are inexpensive and available in large quantity due to natural abundance or widespread use in the chemical or pharmaceutical industries.

All of these materials (save Saccharin, which was unable to be procured in a timely manner), were subjected to a qualitative test for their ability to form a prilled molding powder in the wet slurry process similar to PBX 9501 molding powder. For this qualitative test, no attempts were made to use a particle size distribution of starting material equivalent to the Class I and Class II HMX in PBX 9501,<sup>6</sup> except in the cases of the barium sulfate and magnesium hydroxide, both of which were available in the requisite sizes.

Because dynamic mocks rely on volumetric flow of the binder system at various temperatures under load, it was decided to replicate the volume rather than the weight of binder in PBX 9501. The widely varying densities of the substrates and their dissimilarities from that of HMX called for the weight percent of each system to be adjusted to match the volume percentage of the binder system to PBX 9501 (7.4 % v/v). The corresponding weight percentages for a volume match for each binder system are presented in Table 1.

This qualitative screening showed viability of eight candidate materials through the wet slurry process. Two others, theobromine and thiouracil, appeared to coat but not form prilled molding powder, and three that failed to form prills in the wet slurry process (magnesium hydroxide, glycouril, and theobromine) were successfully prilled through a new resonant acoustic mixing (RAM) process.<sup>7</sup> These results are noted in Table 1. Because of the success of the RAM process, water insolubility of the substrate material was not made a strict requirement since materials that failed in the wet slurry could potentially be handed off to the RAM process for further evaluation.

The first successful formulation was with 1,5-dinitronaphthalene (DNN). It formed irregularly shaped, orange-colored prills (Figure 1).



Figure 1. Prills of candidate DNN mock.

**Table 1.** Candidate mock materials and properties.

Material	Category	Uses	Binder (% w/w)	Crystal m.p. (°C)	Crystal TMD (g/cm <sup>3</sup> )	Mock TMD (g/cm <sup>3</sup> )	Prilled molding powder? (Y/N)	Notes
PBX 9501	Reference	Explosive	5.00 <sup>6</sup>	276 <sup>9</sup>	1.905 <sup>9,10</sup>	1.86 <sup>9</sup>	Y	
Barium sulfate	Inorganic	Mineral, imaging, fracking	2.23	1580 <sup>3</sup>	4.49 <sup>3</sup>	4.252	N	
Magnesium hydroxide	Inorganic	Mineral, pharmaceutical	4.18	350 <sup>3</sup>	2.34 <sup>3</sup>	2.266	N	Successful via RAM. <sup>7</sup>
Sodium hexafluoroaluminate	Inorganic	Mineral	3.41	1013 <sup>3</sup>	2.9 <sup>3</sup>	2.780	N	
Acetamidophenol (Tylenol)	Organic	Pharmaceutical	7.33	207–209 <sup>3</sup>	1.293 <sup>11</sup>	1.292	N	
Anthracene	Organic	Petroleum byproduct	7.59	217–218 <sup>3</sup>	1.245 <sup>12</sup>	1.248	N	
Bis(hydroxyphenyl) sulfone	Organic	BPA replacement for cans	6.80	240.5 <sup>8</sup>	1.402 <sup>13</sup>	1.393	Y	Significant holdup on vessel after formulation.
Caffeine	Organic	Pharmaceutical, natural product	6.64	237 <sup>8</sup>	1.438 <sup>14</sup>	1.426	N	
Carbanilide (diphenyl urea)	Organic	Horticulture	7.61	238 <sup>3</sup>	1.243 <sup>15</sup>	1.246	N	Prills form initially, then fall apart during quench.
Carbazole	Organic	Pharmaceutical	7.29	244.8 <sup>8</sup>	1.301 <sup>16</sup>	1.299	N	
Cyanuric acid	Organic	Swimming pools	5.44	> 360 <sup>3</sup>	1.778 <sup>17</sup>	1.741	N	
Dihydroxybenzophenone	Organic	Chemical feedstock	7.11	210 <sup>3</sup>	1.336 <sup>18</sup>	1.332	Y	
1,5-Dihydroxynaphthalene	Organic	Dye precursor	6.76	262 (dec.) <sup>3</sup>	1.412 <sup>19</sup>	1.402	Y	
1,5-Dinitronaphthalene	Organic		6.09	216 <sup>3</sup>	1.578 <sup>20</sup>	1.556	Y	Parent material has isomeric impurity and toxicity issues.
Glycine anhydride	Organic		6.04	312 (dec.), 260 (subl.) <sup>3</sup>	1.591 <sup>21</sup>	1.568	N	
Glycouril	Organic	Chemical feedstock	6.00	300 (dec.) <sup>3</sup>	1.604 <sup>22</sup>	1.580	N	Successful via RAM. <sup>7</sup>
Guanine	Organic	Natural product	5.78	360 (dec.) <sup>3</sup>	1.667 <sup>23</sup>	1.638	N	
Indigo	Organic	Dye, natural product	6.48	390 (subl. 300) <sup>3</sup>	1.477 <sup>24</sup>	1.462	Y	Dark blue color.
Methyl gallate	Organic	Natural product	6.45	202 <sup>3</sup>	1.483 <sup>25</sup>	1.468	N	
Phthalamide	Organic		6.51	228 <sup>26</sup>	1.21 <sup>26</sup>	1.215	N	
Phthalimide	Organic	Chemical feedstock	7.80	238 <sup>3</sup>	1.47 <sup>27</sup>	1.456	Y	Sandy prills.
Phthalylsulfathiazole	Organic	Pharmaceutical	6.01	272 (dec.) <sup>3</sup>	1.6 <sup>28</sup>	1.576	N	
Sulfobenzimide (Saccharin)	Organic	Artificial sweetener	N/A	225–228 <sup>3</sup>	1.605 <sup>29</sup>	1.581	N	
Theobromine (chocolate)	Organic	Natural product	6.29	330 (subl. 290) <sup>3</sup>	1.524 <sup>30</sup>	1.506	N	Material coats, but does not form prills. Successful in RAM. <sup>7</sup>
Theophylline	Organic	Pharmaceutical, natural product	6.56	270–274 <sup>3</sup>	1.458 <sup>31</sup>	1.445	N	
Thiouracil	Organic	Pharmaceutical	5.94	> 340 <sup>3</sup>	1.62 <sup>32</sup>	1.595	N	Material coats, but does not form prills.
Thymolphthalein	Organic	Dye, indicator	7.94	253 <sup>3</sup>	1.187 <sup>33</sup>	1.194	Y	
Vanillic acid	Organic	Foodstuffs	6.57	207 <sup>3</sup>	1.456 <sup>34</sup>	1.443	Y	

The parent material was received as hard, light orange prills of agglomerated crystals, necessitating manual grinding prior to formulation, a time-consuming process. It met the melting point criteria (216 °C)<sup>3,8</sup> and crystallized into monoclinic (P2<sub>1</sub>/a) hexagons.<sup>3,20</sup> However, the substrate suffered from toxicity issues (LD<sub>50</sub> = 86 mg/kg),<sup>8</sup> and the presence of an isomeric impurity. This isomer, 1,3-dinitronaphthlene, had a lower melting point than desired (146–148 °C),<sup>35</sup> a different density (1.528 g/cm<sup>3</sup>)<sup>36</sup> that led to difficulty in determining theoretical maximum density (TMD), a problematic crystal system (triclinic), and a poor crystal type (needles). For all of these reasons, DNN was discarded as a serious mock candidate.

The second mock candidate was prepared from indigo. A very low toxicity (LD<sub>50</sub> > 5000 mg/kg),<sup>37</sup> high melting point (390 °C),<sup>3</sup> and monoclinic (P2<sub>1</sub>/c) parallelepiped crystals recommended it.<sup>24</sup> As the world's oldest dye that is produced synthetically as well as extracted from plants, it is ubiquitous and inexpensive on large scale (\$1.50–3/lb.) and has voluminous crystallographic and material property information available. As a stand-in for HMX, it has a  $\beta$  polymorph that shares the same space group (P2<sub>1</sub>/n),<sup>38,39</sup> very similar solubility in water and organic solvents, and forms well-shaped prills through the wet slurry process. Unfortunately for this investigation, it is a powerful chromophore, appearing almost black (Figure 2), precluding it from accepting any dyes, and therefore excluding it from further consideration based on the second criteria.



**Figure 2.** Prills of candidate indigo mock.

The indigo and DNN mock candidates were prepared before the color criteria was added, making these two the most highly colored materials. Although ineligible for the current investigation, future mock candidates made from indigo may bear further exploration for other uses in which its color is not prohibitive.

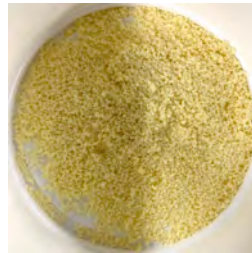
After the color criteria was added, phthalimide was successfully formulated. This material melts at 238 °C,<sup>3</sup> can be crystallized as prisms, and was available widely as a chemical feedstock. Formulation resulted in a coated crystalline material that could generously be described as poor quality, irregular, fragile prills (Figure 3).



**Figure 3.** Prills of candidate phthalimide mock.

Formulation of the material was otherwise unremarkable, forming a normal biphasic system. The color, low toxicity (LD<sub>50</sub> > 5000 mg/kg)<sup>40</sup> and low cost of phthalimide all meet criteria, but the quality of the formulated material renders it nearly unusable.

The light-colored bis(hydroxyphenyl)sulfone (BHPS) was formulated next. The base material met the main criteria of melting point (240.5 °C),<sup>8</sup> crystal habit system and type (orthorhombic C-2bc2 bipyrimidal or prisms),<sup>15</sup> and off-white color. The prills formed were small and irregularly shaped (Figure 4).



**Figure 4.** Prills of candidate BHPS mock.

The wet slurry process for this material was difficult and appeared to suffer from solubility issues of BHPS in the lacquer solvent, methyl ethyl ketone (MEK). This was evident not only from the lack of organosol formation (Figure 5), but also from the significant holdup on the vessel and stirrer after quenching (lowering yield). Although BHPS itself has a reasonably high LD<sub>50</sub> (1600 mg/kg),<sup>8</sup> this compound is an estradiol mimic in the body and can be absorbed through the skin, so toxic effects can begin at as low as 200 mg/kg, creating a potential hazard for the worker. Ironically, BHPS, also called BPS, or bisphenol S, is a replacement for the notorious bisphenol A as a liner for steel food cans and water bottles. It is therefore available inexpensively as a large commodity, but its biologic effects call into question its long-term use and thus long-term availability, so, coupled with the difficulty in processing and low yield, this compound was abandoned.



**Figure 5.** Candidate BHPS mock in process. Note the lack of phase separation or organosol formation.

The attempt at formulation of dihydroxybenzophenone (DHBP) produced small, well-formed prills that exhibited a similar color to PBX 9501 (Figure 6).



**Figure 6.** Prills of candidate DHBP mock.

The melting point (210 °C),<sup>3</sup> crystal system and type (monoclinic P2<sub>1</sub>/c blocks),<sup>18</sup> and reasonable toxicity (LD<sub>50</sub> > 500mg/kg)<sup>41</sup> are all desired characteristics. The cost on large scale was reasonable, likely due to the use of DHBP in cosmetics, plastics, and films, but it was somewhat expensive on small-scale (\$0.91/g). Formulation of this material was not straightforward, and similar to the process with BHPS, yields were poor due to holdup of material on the vessel and some remaining fines. Although not ideal, this was the first mock candidate prepared that had potential for scale-up studies.

Thymolphthalein, an indicator changing color above pH 9.3–10.5 from colorless to blue, formulated reasonably well. This candidate mock, pictured in Figure 7, was made of well-formed round prills and had an off-white color. Thymolphthalein has been used as an indicator, a laxative, and in disappearing ink, so is available in reasonable quantities and prices.





**Figure 7.** Candidate thymolphthalein mock.

The parent material melts at 253 °C,<sup>3</sup> can crystallize as prisms, and has a low toxicity (LD<sub>50</sub> = 2260 mg/kg).<sup>33</sup> While not a particularly high priority, the low density of the unbound material (1.187 g/cm<sup>3</sup>)<sup>33</sup> leads to some issues with buoyancy and thus non-trivial wetting and formulating, although a biphasic system with a clear supernatant forms. This material is equivalent in quality to the candidate mock produced from 1,5-dihydroxynaphthalene (*q.v.*), but has superior color. The differing properties of these two materials may lend to one or the other being superior for a specific application.

Another promising candidate was produced from 1,5-dihydroxynaphthalene (DHN). As a precursor in the dye industry, DHN is available in large quantity at reasonable cost, with main manufacturing sites in India and China. Formulation was particularly facile and excellent quality prills mimicking size and morphology of PBX 9501 were prepared with ease (Figure 8).



**Figure 8.** Prills of candidate DHN mock.

Pure DHN is listed on manufacturer's websites and in reference books as a white crystalline material, but, as evidenced by the formulated material in Figure 7, the starting material as received was a grey color. Hoping to avoid the colored impurity in that particular lot, DHN from another manufacturer was procured. This had a light pink color but appeared to be less heavily colored than the previous lot. After formulation, the color was more evident, producing a pink colored material (Figure 9).



**Figure 9.** Pink prills of candidate DHN mock.

Pure DHN melts at 262 °C,<sup>3</sup> is the same monoclinic P2<sub>1</sub>/n crystal system as β-HMX,<sup>19</sup> can form prisms, and has a reasonable toxicity (LD<sub>50</sub> = 660 mg/kg).<sup>8</sup> These properties and the facility with which quality prills are formed in the same wet slurry process as the parent explosive material recommend its application as a candidate mock material for PBX 9501. Because all mock materials in the DOE are required to be pink unless an exception is granted, the pink color from the second lot of material is not prohibitive, but ideally an uncolored source of the parent DHN could be found to eliminate future coloration consistency issues.

The most promising candidate mock material viable by the wet slurry process was made from vanillic acid. Vanillic acid is an oxidized form of vanillin, and is used not only as a flavoring agent in its own right but also as a precursor to vanillin itself. It is a natural product occurring in such plants as *angelica sinensis* and *euterpe oleracea*,<sup>42,43</sup> is widely available at reasonable cost, and due to its use in foodstuffs necessarily has a very low toxicity (LD<sub>50</sub> = 5020 mg/kg).<sup>44</sup> Vanillic

acid melts at 207 °C<sup>3</sup> and forms monoclinic P2<sub>1</sub>/c crystals.<sup>34</sup> The crystals form as undesirable platelets and needles, but this is a lower priority preferable characteristic. Fortunately, vanillic acid formulates easily and produces high quality prills with a light tan color (Figure 10) that have a faint, pleasant vanilla odor.



**Figure 10.** Quality molding powder of candidate vanillic acid mock.

Based on the experimental results and properties discussed above, the recommended order of further examination of candidate PBX 9501 mocks produced by the wet slurry process is:

1. Vanillic acid
2. (tie) DHN
2. (tie) thymolphthalein
4. DHBP
5. Indigo (for non-color specific applications)

The indigo material could be useful for applications where color is not a requirement, and an undyed version of the thymolphthalein material could potentially serve as an indicator material for operations under basic conditions should such an application arise. All five of these materials are good candidates for PBX 9501 dynamic mocks.

Ideally, future screening of mock materials would be conducted quantitatively by measuring the surface free energy of a given binder (in this case nitroplasticized Estane), the surface free energy of the substrate in question, and then comparing the two for adhesion and delamination strength and stability. This is not a new concept,<sup>45</sup> but all necessary equipment for this capability currently does not exist at LANL. In the future, if appropriate equipment is in place, this may be a more efficient route to new formulations.

## Experimental

### General

Barium sulfate (Haliburton), bis(dinitropropyl)formal/bis(dinitropropyl)acetal (BDNPA/F) (US Navy), bis(hydroxyphenyl)sulfone (TCI), caffeine (Alfa), carbanilide (TCI), 4,4'-dihydroxybenzophenone (TCI), 1,5-dihydroxynaphthalene (Alfa, TCI), 1,5-dinitronaphthalene (TCI), Estane 5703 (BF Goodrich), glycine anhydride (TCI), glycouril (Acros), guanine (Alfa), indigo (ProChemical), Irganox 1010 (Aldrich), magnesium hydroxide (Garrison Minerals), methyl ethyl ketone (MEK) (Fisher), methyl gallate (TCI), phthalamide (TCI), phthalimide (TCI), sodium hexafluoroaluminate (Fisher), theobromine (TCI), thiouracil (Acros), thymolphthalein (Acros), and vanillic acid (Alfa) were used as received. Weights were measured on a Mettler Toledo AG285 balance.

### Example Formulation of Indigo

A lacquer of Estane 5703 (1.9 g), BDNPA/F (1.9 g), and Irganox 1010 (0.8 g) was prepared by dissolution in MEK (70 mL). This lacquer was added to a stirred slurry of indigo (46.1 g) in water (170 mL) thermostated to 45 °C. After approximately 5 min, the material began to agglomerate. Agglomeration was allowed to continue stirring until prills had fully formed at approximately 12 min, then was quenched with water (340 mL), vacuum filtered through a GF/B filter, allowed to air dry and then oven dried at 60 °C overnight.

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